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SYNTHESIS OF CATALYTIC COBALT-CONTAINING COATINGS ON ALLOY AL25 SURFACE BY PLASMA ELECTROLYTIC OXIDATION

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The study aims at the investigation of the influence of electrolyte composition and plasma electrolytic oxidation modes on the composition and morphology of a mixed aluminum and cobalt oxides at the AL25 alloy. Composition, morphology and surface roughness of the oxide systems are examined by scanning electron microscopy, X-ray analysis and atomic force microscopy. Mixed oxide coatings $Al_2O_3{\cdot}CoO_x$ formed from the diphosphate electrolytes at various concentration ratio diphosphate / cobalt sulfate contain cobalt of 8–30 at. % (in terms of metal) in the matrix of alumina. Plasma electrolytic oxidation in a two-stage mode of the incident power provided formation of strongly adhered coatings characterized by non-stoichiometry ratio of cobalt and oxygen as well as low content of silicon in deposits. Obtained mixed oxide systems have developed surface with alternating the spheroid and torus-shaped structures which is associated with a large number of catalytic sites. They exhibit catalytic behavior in the model reactions of CO conversion to CO_2 and benzene oxidation not inferior to the contacts with noble metals. The coatings $Al_2O_3{\cdot}CoO_x$ contribute to fuel economy and improve the environmental performance of the internal combustion engine thus can be recommended for use in the neutralization of gas emissions systems and as coatings for pistons of combustion chamber.

Keywords: *AL25 alloy, cobalt oxides, plasma electrolytic oxidation, mixed oxide system, surface morphology, catalytic activity*

Environmental and technical problems accompanying the operation of internal combustion engines (ICE) are associated with the incomplete combustion of fuel and, respectively, the inevitable formation of toxic components (CO, NO_x, and soot). One of the perspective ways to improve the performance of ICE can be the use of catalysis *in situ* in the combustion chamber [1]. Catalytic processes are characterized by lower activation energies and consequently temperatures of the fuel burning start as well as its higher completeness [2]. These lead to a decrease in the maximum pressure in the combustion chamber and, hence, in the severity of engine operation and to the minimization of emissions of hazardous substances with exhaust gases.

The currently available hydrocarbon fuel combustion catalysts are divided into two groups: catalysts based on noble metals (most commonly Pd and Pt) and transition-metal oxides (Mn, Co, Fe, *etc*.), particularly those with a complex composition [3]. At high temperatures, significant advantages are shown by a family of catalysts based on *d*-metals, in particular, cobalt oxides, which exhibit thermal lability and high oxygen affinity [4]. Non-stoichiometric cobalt oxides not only provide the thermal stability of the catalysts but also lead to a significant improvement of its reactivity.

In terms of rational designing and effective technology, it seems appropriate to deposit a catalytic layer directly on the surface of ICE pistons manufactured using AL25 alloys with an optimal combination of physico-mechanical and performance properties [5]. The most promising method for the formation of thin layers on aluminum alloys, in particular, silumins, is plasma electrolytic oxidation (PEO). This method provides the incorporation of catalytically active components into an alumina matrix owing to the implementation of both electrochemical and thermo-chemical reactions in high-energy modes [6, 7]. However, it should

be taken into account that the PEO of silumins is complicated because these materials contain a large number of alloying components and intermetallic compounds with different chemical properties of oxides. Previously, we have shown the PEO expediency of the AL25 alloys in a diphosphate solution with addition of manganese salts to produce mixed manganese and aluminum oxides of different compositions. On this basis, the aim set in this paper is a study of the electrolyte composition and the PEO modes for the formation of a mixed oxide layer with high cobalt content on the surface of the AL25 alloy.

EXPERIMENTAL

The studies were conducted using AL25 alloy samples with the working surface of 2.0 cm^2. The concentration of alloying elements in a substrate, wt. %: Si – 11.0–13.0, Cu – 1.5–3.0, Ni – 0.8–1.3, Mg – 0.8–1.3, Mn – 0.3–0.6, Fe<0.8, Zn<0.5, Ti<0.2, Cr<0.2, Pb<0.1. The surface preparation included sequential procedures of mechanical grinding, etching in an alkaline solution, thorough washing with distilled water, and drying. Electrolyte solutions for the pretreatment and PEO were prepared from certified reagent-grade reactants and distilled water.

The PEO of samples with a working surface of 2 cm^2 was conducted using a B5-50 stabilized power supply that maintained voltage up to 300 V. PEO was implemented in an electrolytic cell under conditions of forced cooling of the electrolyte to the temperature of 20–30 °C at a current density varied in the range of I = 2–10 A/dm^2 up to final formation voltage 180–235 V; duration of oxidation process was of 40–60 min. PEO was implemented from working electrolytes composition, g/l: $K_4P_2O_7$ – 65.0–300.0; $CoSO_4$ – 7.5–46.5.

The chemical composition of the coatings was determined by X-ray photoelectron spectroscopy on an INCA Energy 350 energy dispersive spectrometer; X-ray radiation was excited via exposing the samples to a 15-keV electron beam. In addition, X-ray fluorescence analysis was conducted using a SPRUT portable spectrometer with a relative standard deviation of 10^{-3}–10^{-2}; the error in determining the component content was ±1 wt. %. The surface morphology of the coatings was studied using a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were recorded by the registration of secondary electrons (BSEs) via scanning with an electron beam; this mode made it possible to study the morphology with a high resolution and contrast ratio. The surface roughness was evaluated by the contact method on 10 × 10 × 2 mm samples with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2 and 0.2 nm, respectively; 1024 × 1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm).

The catalytic properties of the resulting oxide systems were studied in the model reaction of carbon monoxide conversion to carbon dioxide [8]. In addition, the catalytic properties of the materials were studied in the flameless oxidation of benzene with air [9].

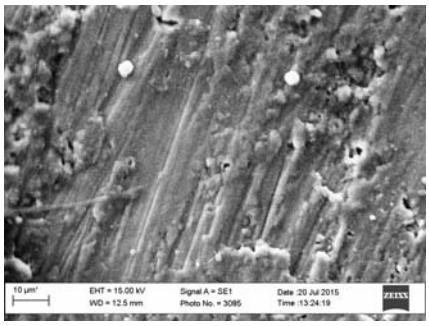
RESULTS AND DISCUSSION

The results of experimental studies show that PEO process of alloy AL25 in diphosphate electrolytes containing cobalt (II) is a classic case [10]. Simultaneous progress of electrochemical oxidation and thermal decomposition of electrolyte components implemented in the mode of PEO contributes high adhesion of an oxide coating to the substrate and incorporation of catalytic component – cobalt oxides. Composition of multicomponent oxides depends on both the concentration ratio of the electrolyte components and the oxidation current density. Thus, the oxide system is logically enriched with cobalt by increasing its content in the solution, but the electrolyte stability as well as service time is reduced. At the same time, increasing the diphosphate concentration in the bath is not desirable because it leads to a decrease of PEO efficiency.

It was also found that the cobalt content in mixed oxide coatings increases when PEO is performed in the incident power mode. Starting current density i_1 is higher for forming barrier aluminum oxide film on the AL25 substrate, which is accompanied by oxidation of the alloying components and particularly silicon with soluble substances forming and promotes homogenization of the alloy surface [11]. After the process enters a mode of stable arcing current density for the second stage, i_2 is reduced to ensure the formation of the mixed oxide layer. The current density for the first PEO stage in cobalt-diphosphate solution does not exceed the interval 8–10 A/dm^2, while the second stage is

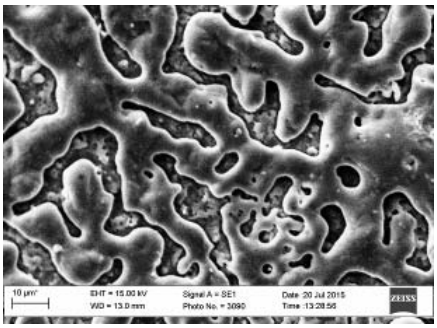
advisable to hold at current density of 2.5–3.0 A/dm^2. Characteristic parameters of voltage PEO process also depends on the composition of the electrolyte: arcing voltage U_i is 115–120 V, and the resulting formation voltage U_k is 140–160 V. It should be noted that all voltage parameters grow with the electrolyte dilution and with increasing current density as well as the cobalt content in the mixed oxides increases with the current density and uniformity of its distribution on the surface is improved [12].

Surface morphology and composition of PEO coatings doped with cobalt oxides depends on both the concentration of electrolyte and oxidation conditions – current density, voltage and time of formation (Fig. 1). The incorporation of the cobalt in oxide systems affects the formation of separate spheroid islets of characteristic blue-purple color. During the treatment the number of islet structures significantly increases, some the islets grow together, agglomerated and form a ceramic like mosaic patterns (Fig.1 *b*, *c*). The higher content of cobalt, the more developed but at the same time the less uniform is the surface of coating. Formed oxide systems have high developed microglobular surface [13] with cobalt content 8–30 at. % and lower concentration of impurities comparing with Al │Al_2O_3 coating synthesized in pure diphosphate electrolyte (Fig. 1 *a*), which is essential for the high catalytic properties of the material [3]. Analysis of the composition of oxide systems indicates nonstoichiometric ratio of cobalt and oxygen which is favorable for the implementation of catalytic processes involving oxygen.



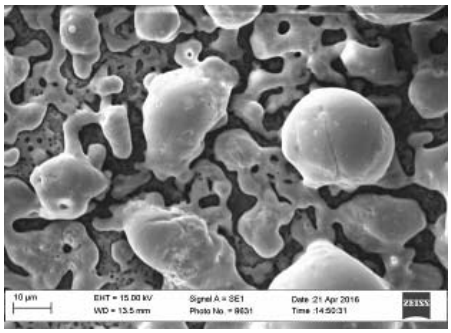
Al – 40.5; O – 53.7;
Si – 5.4; Mn – 0.4

a



Al – 33.3; Co – 8.7;
O – 55.2; Si – 2.8

b



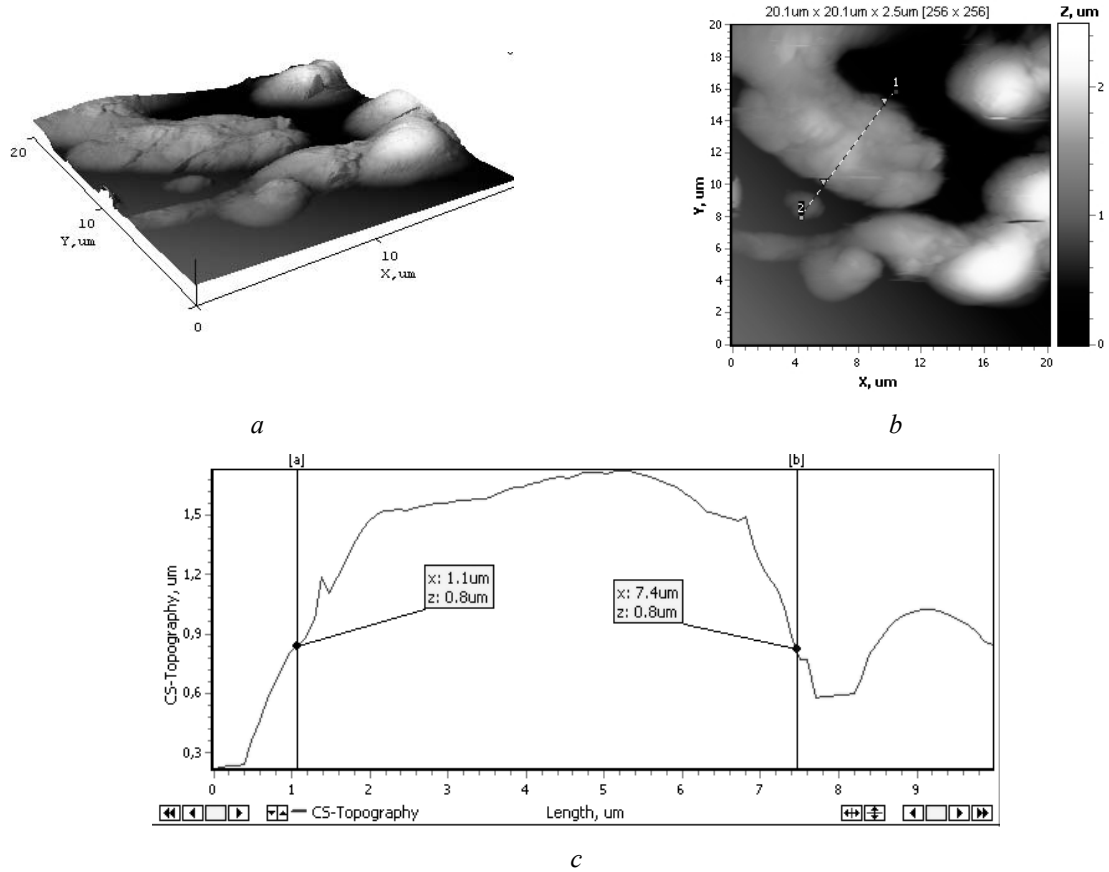
Al – 48.7; Co – 23.6;
O – 25.9; Si – 1.8

c

Fig. 1. Surface morphology and composition (at. %) of PEO coatings on AL25: *a* – Al │Al_2O_3 obtained in electrolyte 200 g/l $K_4P_2O_7$ with current density i_1=8 A/dm^2; mixed oxide systems Al │Al_2O_3·CoO_x obtained in PEO two stage modes (i_1=8 A/dm^2, i_2=2.5 A/dm^2) in diphosphate electrolyte with addition of $CoSO_4$ of concentration, g/l: *b* – 10; *c* – 30. Magnification 1000

It has been found by AFM analysis that the surface morphology of $Al \mid Al_2O_3 \cdot CoO_x$ system with cobalt content of 8–12 at. % (Fig. 2) is characterized by the high roughness and large grain size. Mixed oxide coatings are composed from the set of spheroid grains with an average size of 1–2 μm which gather and form the parts of smooth surface with the spherical grain agglomerates of 6–8 μm (Fig. 2 *a*). The surface roughness may be characterized with the spread of grain size on the cross section between markers 1–2 (Fig. 2 *b*). In addition, the surface morphology of oxides is characterized by rather large difference between hills and valleys (Fig. 2 *c*) of 0.3 μm up to 1.2 μm and alternating the spheroid and torus-shaped structures (Fig. 1 *c*).

Testing of the synthesized oxide systems in the model reaction of CO conversion to CO_2 has shown that the ignition temperature is 230 °C and the complete conversion is achieved at 305 °C which is comparable with the characteristics of platinum catalysts 217 °C and 297 °C respectively [8]. Completeness of model reaction of flameless oxidation of benzene over $Al \mid Al_2O_3 \cdot CoO_x$ catalyst is higher than that over palladium-containing catalysts. For instance, the degree of benzene oxidation, which is determined by the amount of resulting CO_2, for example, at the temperature of 300 °C, is 5.0 times higher [8]. Tests of developed materials based on mixed oxide systems in model reactions of CO and benzene oxidation have shown that their catalytic activity is not inferior to the contacts that contain noble metals. This can be attributed to several factors: firstly due to a high affinity of non-stoichiometric cobalt oxides to oxygen and the corresponding decrease in the activation energy of double bonds O=O destruction [14]. Secondly, the developed microglobular surface of oxide systems is characterized by a large number of catalytic centers and provides an increase in the number of elementary collisions and interactions in multicomponent systems.



a *b*

c

Fig. 2. 3D- (*a*) and 2D (*b*) maps of the surface and cross sections profile (*c*) between markers 1 and 2 for mixed oxide system $Al \mid Al_2O_3 \cdot CoO_x$ with cobalt content 8.7 at. %. Scanning area 20×20 μm

Pilot tests of mixed oxides deposited on the surface of combustion chambers piston of the ICE, showed a reduction in fuel consumption at 1–3 % and NO_x emissions reduction at forced diesel engine operating modes. This is due to lower the ignition temperature of the air-fuel mixture on the surface of $Al\,|\,Al_2O_3{\cdot}CoO_x$ catalyst composed of non-stoichiometry oxides with developed surface.

Thus we can conclude that the varying electrolyte concentration and conditions of the PEO process allows formation of oxide coatings of different composition and morphology that are expected to affect their functional properties including catalytic activity in the process of burning fuel in internal combustion engines and reduce the toxicity of emissions improving fuel efficiency and environmental performance of engines [15].

CONCLUSIONS

(i) Mixed oxide systems $Al_2O_3{\cdot}CoO_x$ with cobalt content of 8–30 at. % were obtained on aluminum alloy AL25 by two step plasma-electrolytic oxidation in a diphosphate electrolyte added with cobalt(II) sulfate. It has been found that surface concentration of silicon dopant in mixed coatings is two to three times less than that in the system $Al\,|\,Al_2O_3$ or treated alloy AL25.

(ii) A nonstoichiometry ratio of cobalt and oxygen in deposits has been shown as well as the cobalt content in mixed oxide increases regularly with concentration of cobalt ions in the electrolyte. At elevated concentrations of cobalt in $Al\,|\,Al_2O_3{\cdot}CoO_x$ the surface morphology changes from the uniformly roughened to microglobular with sufficiently large spheroids.

(iii) Obtained mixed oxide systems have developed surface with alternating the spheroid and torus-shaped structures which is associated with a large number of catalytic sites. They exhibit catalytic behavior in the model reactions of CO conversion to CO_2 and benzene oxidation not inferior to the contacts with noble metals. The coatings $Al_2O_3{\cdot}CoO_x$ contribute to fuel economy and improve the environmental performance of the internal combustion engine thus can be recommended for use in the neutralization of gas emissions systems and as coatings for pistons of combustion chamber.

Синтез каталітичних кобальтовмісних покриттів на поверхні сплаву AL25 плазмово-електролітичним оксидуванням

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Розглянуто принципи плазмово-електролітичного оксидування (ПЕО) алюмінієвого сплаву AL25 у дифосфатних лужних розчинах, які містять катіони кобальту(2+). Змішані оксидні системи $Al_2O_3{\cdot}CoO_x$ з вмістом кобальту 8–30 ат. % одержані у двохступінчастому режимі ПЕО. Встановлено, що вміст кобальту в змішаних покриттях $Al_2O_3{\cdot}CoO_x$ закономірно зростає з концентрацією іонів кобальту в електроліті. Морфологія поверхні змішаних оксидів змінюється від рівномірно шорсткої до мікроглобулярної, яка містить великі сфероїди з підвищеним вмістом кобальту. Одержані системи $Al_2O_3{\cdot}CoO_x$ відрізняються розвиненою поверхнею і виявляють каталітичну активність у модельних реакціях конверсії CO у CO_2 та окиснення бензену, що не поступається контактам на основі коштовних металів. Покриття $Al_2O_3{\cdot}CoO_x$ на поверхні поршня сприяють економії палива і покращенню екологічних показників роботи двигунів внутрішнього згоряння.

Ключові слова: *сплав AL25, оксиди кобальту, плазмово-електролітичне оксидування, змішані оксидні системи, морфологія поверхні, каталітична активність*

Синтез каталитических кобальтосодержащих покрытий на поверхности сплава AL25 плазменно-электролитическим оксидированием

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Рассмотрены принципы плазменно-электролитического оксидирования (ПЭО) алюминиевого сплава AL25 в дифосфатных щелочных растворах, содержащих катионы кобальта(2+). Смешанные оксидные системы $Al_2O_3{\cdot}CoO_x$ с содержанием кобальта 8–30 ат. % получены в двухступенчатом режиме ПЭО. Установлено, что содержание кобальта в смешанных покрытиях $Al_2O_3{\cdot}CoO_x$ закономерно возрастает с концентрацией ионов кобальта в электролите. Морфология поверхности смешанных оксидов изменяется от равномерно шероховатой до микроглобулярной, содержащей крупные сфероиды с повышенным содержанием кобальта. Полученные системы $Al_2O_3{\cdot}CoO_x$ имеют развитую поверхность и проявляют каталитическую активность в модельных реакциях конверсии CO в CO_2 и окисления бензола, не уступающую контактам, содержащим благородные металлы. Покрытия $Al_2O_3{\cdot}CoO_x$ на поверхности поршня способствуют экономии топлива и улучшению экологических показателей работы двигателей внутреннего сгорания.

Ключевые слова: *сплав AL25, оксиды кобальта, плазменно-электролитическое оксидирование, смешанные оксидные системы, морфология поверхности, каталитическая активность*

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